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# Condensation of Diethyl Acetonedicarboxylate. I

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Selfcondensation of diethyl acetonedicarboxylate (DADC) using the various catalysts was examined. The analyses of the condensation products of DADC were undertaken by GC and GC–MS. A correlation between the kind of catalysts used and products formed was revealed. Formation of ethyl 4-carboxyorsellinate (**5**) and diethyl 3,5-dihydroxyhomophthalate (**6**) was newly proved in this reaction.

**Keywords**——condensation; diethyl acetonedicarboxylate; magnesium as catalyst; gas chromatography; metal chelated complex; orsellinic acids; coumarin derivatives

As reported previously[2] diethyl 4-carboxy-3,5-dihydroxyhomophthalate (**1**), obtained by a bimolecular condensation of diethyl acetonedicarboxylate (DADC), was used for the synthesis of *dl*-Agrimonolide. Extensive studies on the bimolecular condensation of DADC have been reported by other workers,[3] and the known products may be grouped into two types; one of them are orsellinic acid derivatives, diethyl 4-carboxy-3,5-dihydroxyhomophthalate (**1**) and diethyl 4-ethoxycarbonyl-3,5-dihydroxyhomophthalate (**2**), and the other are coumarin derivatives, 6-ethoxycarbonyl-4,5,7-trihydroxycoumarin (**3**) and 8-ethoxycarbonyl-4,5,7-trihydroxycoumarin (**4**). However, very little information about this reaction mechanism is found in the literature.

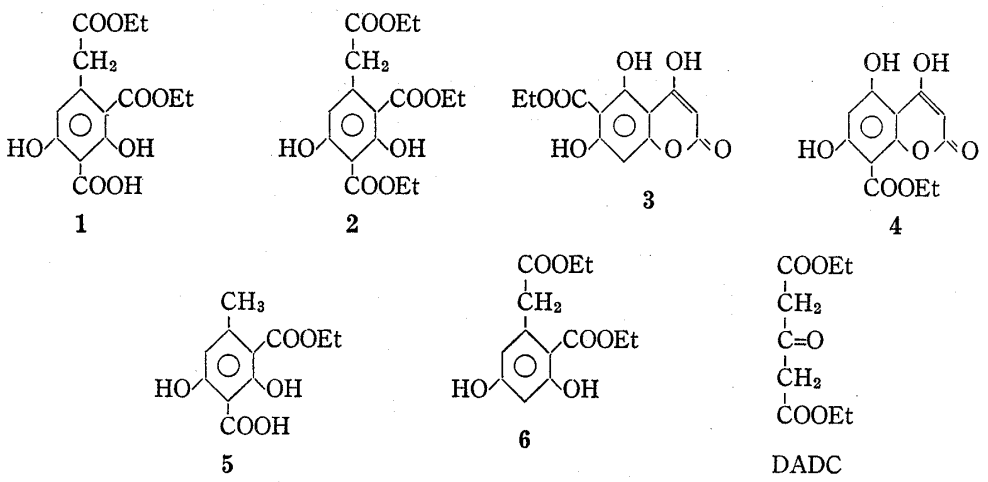


Chart 1

The present study was undertaken to find a more effective catalyst for the selective formation of the product and to elucidate the reaction mechanism. The quantitative and qualititative analyses of individual products in the reaction mixture obtained by heating DADC with various catalysts were carried out by the gas chromatography (GC) and GC-mass

1) Location: *Tsushima-naka 1-1-1, Okayama 700, Japan.*
2) M. Yamato and K. Hashigaki, *Chem. Pharm. Bull.* (Tokyo), **24**, 200 (1976).
3) *a*) D.S. Jerdan, *J. Chem. Soc.*, **75**, 808 (1899); *b*) F.W. Dootson, *J. Chem. Soc.*, **77**, 1196 (1900); *c*) H. Cornelius and H. von Peckmann, *Chem. Ber.*, **19**, 1446 (1886); *d*) A. Sonn, *Chem. Ber.*, **50**, 138 (1917); *e*) W. Gruber, *Chem. Ber.*, **76**, 135 (1943).

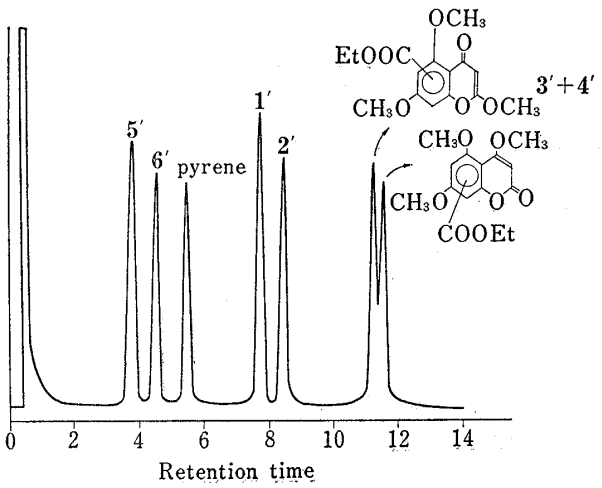


Fig. 1. Gas Chromatogram of Methylated Compounds

(′): Methylated form

spectra. The samples for the analysis were previously methylated with diazomethane. We found the yield of methylation of each sample to be about 90%. The gas chromatogram peaks were compared with those of the purified samples. The peaks of individual methylated compounds were distinguished each other on the gas chromatogram, as shown in Fig. 1. About the formation of positional isomers, **3** and **4**, Gruber[3e] reported that the yield of **3** was 30 times more than that of **4**. We could not separate them and confirm the rate of the formation, but we found the two peaks, **3′** and **4′** on the gas chromatogram in Fig. 1. Those were methylated compounds by diazomethane at 2- or 4-positions of **3** and **4**. Therefore, quantitative analysis of coumarin derivatives, **3** and **4**, is expressed as the sum of the two peaks (**3′** and **4′**).

The results of the reaction using various catalysts are listed in Tables I, II and III. Table I shows the yield of the compounds obtained by the use of metals or their salts as catalyst, Table II that using bases, and Table III that using metals or their salts with ethyl chloroacetate (ECA) as a catalyst.

These results indicated that magnesium powder or zink powder with ECA, was effective for high yield of **1** as a catalyst, and Triton B, sodium ethoxide, and a small amount of magnesium powder or copper powder with ECA, were effective for high yield of **2** as a catalyst.

Table I. Metals and Salts as Catalyst

| Metal | Catalyst (mmol) | | Temp. (°C) | Time (hr) | Yield of products[a] (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | **1** | **2** | **5** | **6** | **3+4** |
| Mg | Mg | 51 | 170—180 | 0.6 | 1.7 | 10.7 | 1.0 | 3.0 | — |
| | MgO | 35 | 160 | 0.5 | 5.2 | 0.6 | 2.5 | 1.4 | — |
| | $Mg(OH)_2$ | 51 | 150 | 1.5 | 6.2 | — | 6.2 | 1.5 | — |
| | $MgSO_4$[b] | 51 | 130 | 3.5 | — | — | — | — | — |
| | $MgCl_2 \cdot 6H_2O$ | 24 | 110 | 2.5 | 5.6 | — | 2.6 | — | — |
| | $MgCl_2$ | 50 | 140—160 | 0.5 | 3.1 | — | 1.1 | — | — |
| Al | Al | 17 | 160—180 | 1.5 | — | — | — | — | — |
| | $Al_2O_3$ | 24 | 180—220 | 3.0 | 1.9 | 4.3 | — | — | — |
| | $AlCl_3$ | 30 | 60—120 | 0.5 | 14.5 | 1.6 | 5.8 | — | — |
| Ca | Ca | 50 | 160—165 | 0.5 | 2.5 | 22.6 | 0.5 | 8.7 | — |
| | $Ca(OH)_2$[c] | 50 | 110 | 2.0 | — | — | — | — | — |
| | $CaCl_2$ | 69 | 160—180 | 0.5 | 3.8 | 8.0 | 1.1 | 21.7 | — |
| | CaO | 53 | 170 | 0.8 | 0.6 | 1.3 | 1.2 | 6.2 | — |
| K | K[c] | 69 | 110 | 2.5 | — | — | — | — | — |
| Na | Na | 87 | 80—120 | 0.2 | 2.6 | 10.4 | — | — | — |
| | Na | 87 | 130—180 | 0.2 | 1.5 | 6.2 | — | — | — |
| | Na[c] | 87 | 110 | 0.5 | 3.0 | 0.4 | — | — | 4.7 |

*a*) Each yield was obtained from 24.75 mmol of DADC.
*b*) In xylene 25 ml.
*c*) In toluene 25 ml.

Table II. Bases as Catalyst

| Catalyst (mmol) | | Temp. (°C) | Time (hr) | Yield of products[a] (%) 1 | 2 | 5 | 6 | 3+4 |
|---|---|---|---|---|---|---|---|---|
| Triethylamine | 0.7 | 180—190 | 2.5 | 1.1 | 8.1 | — | 1.4 | — |
| Triton B | 0.2 | 180 | 2.5 | 1.5 | 10.4 | — | 2.1 | — |
| $Mg(OEt)_2$ | 21 | 140—180 | 1.0 | 0.4 | 0.3 | — | — | — |
| $Mg(OEt)_2$[b] | 21 | 110 | 3.5 | 0.3 | 1.7 | — | — | — |
| $Al(OC_3H_7)_3$ | 30 | 95—160 | 8.0 | — | — | — | — | — |
| *t*-BuOK[b] | 69 | 85 | 10.0 | — | — | — | — | — |
| NaOEt | 63 | 180 | 2.5 | 2.2 | 10.4 | — | — | 10.2 |
| NaOEt[b] | 94 | 110 | 1.5 | — | — | — | — | 60.0 |

a) Each yield was obtained from 24.75 mmol of DADC.
b) In toluene 40 ml.

Table III. Ethyl Chloroacetate with Metal or Salt as Catalyst

| Catalyst (mmol) | | | | Temp. (°C) | Time (hr) | Yield of products[a] (%) 1 | 2 | 5 | 6 | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| ECA | 8.16 | Mg | 51.4 | 160—180 | 0.4 | 30.1 | 4.1 | 5.7 | 1.5 | 41.4 |
| ECA | 0.41 | Mg | 1.2 | 180 | 3.0 | 1.1 | 33.0 | 0.8 | 5.1 | 40.0 |
| ECA | 8.16 | Ca | 49.9 | 180 | 0.5 | 8.0 | 6.3 | 1.3 | 9.2 | 24.8 |
| ECA | 8.16 | Cu | 52.0 | 140—160 | 1.0 | 1.6 | 13.6 | — | 1.3 | 16.5 |
| ECA | 8.16 | Zn | 15.3 | 180 | 1.0 | 18.7 | 9.5 | 4.4 | 2.6 | 35.2 |
| ECA | 8.16 | | | 180—190 | 3.5 | — | 6.1 | — | — | 6.1 |
| ECA | 8.16 | $MgCl_2$ | 50.4 | 140 | 1.0 | 1.2 | — | 1.1 | 3.7 | 6.0 |
| ECA | 0.41 | $MgCl_2$ | 50.4 | 160—170 | 2.0 | 2.0 | — | — | 4.4 | 6.4 |

a) Each yield was obtained from 24.75 mmol of DADC.

The coumarin derivatives, **3** and **4**, were obtained in a high yield by the use of sodium ethoxide in an inert solvent such as toluene.

The formation of ethyl 4-carboxyorsellinate (**5**) and diethyl 3,5-dihydroxyhomophthalate (**6**) were proved in the condensation of DADC. These were elucidated by the following fact, that is, the unknown two peaks detected on the gas chromatogram of methylated reaction mixture were identified as ethyl 3,5-dimethyl-4-methoxycarbonylorsellinate (**5'**), and diethyl 3-hydroxy-5-methoxyhomophthalate (**6'**). These were confirmed by elemental analyses, NMR spectra, and mass spectra. When the catalyst effective for the high yield of **1** was used, a small amount of **5** was formed, and similarly, a small amount of **6** accompanied the main product **2** when DADC was treated under the condition for the high yield of **2**. As mentioned above, the selective formation of **1** or **2** depends on the kind of a catalyst. Particularly, when magnesium powder and ECA are used as a catalyst, the relative amount of magnesium and ECA to the fixed amount of DADC seemed to be an important factor to control the formation of either **1** and **5** or **2** and **6**. For instance, when 1.25 g (51.14 mmol) of magnesium powder and 1.0 g (8.16 mmol) of ECA were used for 5.0 g (24.75 mmol) of DADC, **1** was formed as a main product, while the use of 0.03 g (1.23 mmol) of magnesium powder with 0.05 g (0.41 mmol) of ECA for 5.0 g (24.75 mmol) of DADC resulted in the formation of **2** as a main product. It was noted that the sum of the yields of these orsellinic acids (**1**, **2**, **5**, and **6**) was nearly constant, and the sum of the yield of **2** and **6** decreased with increasing the yield of **1** and **5**. Evidently, the yield of two set of products was complementary.

The experimental results for the relationship between the yield of these orsellinic acids (**1**, **2**, **5**, and **6**) and the amount of magnesium powder and ECA for 5.0 g (24.75 mmol) of DADC are shown in Table IV and in Fig. 2, and 3. Fig. 2 shows the relationship between

Table IV. Correlation between the Yield of the Products and Used Amount of Magnesium and ECA as Catalyst

| Mg (mmol) | ECA (mmol) | Time | Temp. (°C) | Yield of product[a] (%) 1 | 2 | 5 | 6 | Total |
|---|---|---|---|---|---|---|---|---|
| 51.44 | 0.00 | 1.0 hr | 170—180 | 1.7 | 10.7 | 1.0 | 3.0 | 16.4 |
| 51.44 | 0.41 | 40 min | 170—180 | 4.4 | 31.3 | 5.7 | 1.5 | 42.9 |
| 51.44 | 2.61 | 40 min | 170—180 | 16.6 | 8.5 | 2.9 | 3.5 | 31.5 |
| 51.44 | 4.17 | 35 min | 170—180 | 22.5 | 4.8 | 3.0 | 1.7 | 32.0 |
| 51.44 | 6.21 | 25 min | 170—180 | 25.5 | 5.3 | 4.6 | 2.5 | 37.9 |
| 51.44 | 8.16 | 20 min | 170—180 | 30.1 | 4.1 | 5.7 | 1.5 | 41.4 |
| 51.44 | 16.34 | 20 min | 170—180 | 34.1 | 1.5 | 4.4 | 1.1 | 41.1 |
| 0.00 | 8.16 | 3.5 hr | 180—190 | — | 6.1 | — | — | 6.1 |
| 1.23 | 8.16 | 3.0 hr | 180 | 6.7 | 27.8 | 0.6 | 3.9 | 39.0 |
| 4.12 | 8.16 | 3.0 hr | 180 | 19.6 | 6.5 | 3.2 | 3.4 | 32.7 |
| 12.34 | 8.16 | 40 min | 170 | 26.9 | 4.3 | 3.5 | 2.4 | 37.1 |
| 24.69 | 8.16 | 25 min | 170 | 27.9 | 3.5 | 3.4 | 1.5 | 36.3 |
| 37.04 | 8.16 | 25 min | 170 | 26.0 | 2.4 | 3.0 | 2.0 | 33.4 |
| 45.27 | 8.16 | 20 min | 170 | 24.6 | 2.9 | 3.0 | 1.4 | 31.9 |
| 51.44 | 8.16 | 20 min | 160—180 | 30.1 | 4.1 | 5.7 | 1.5 | 41.4 |

a) Each yield was obtained from 24.75 mmol of DADC.

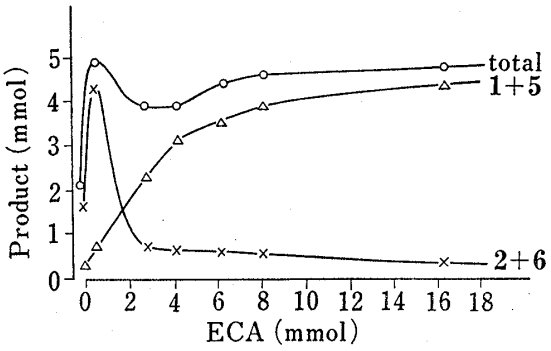


Fig. 2. Quantitative Correlation between the Products and Used Amount of ECA (DADC; 24.75 mmol Mg; 51.44 mmol)

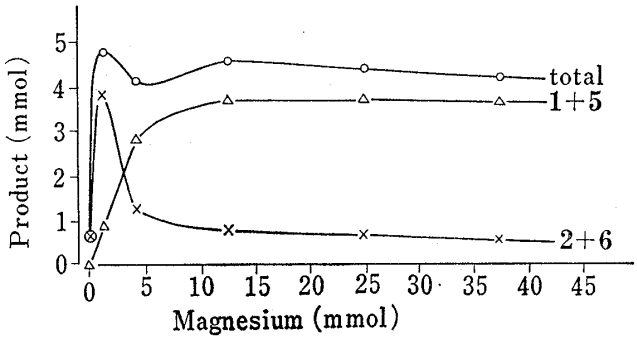


Fig. 3. Quantitative Correlation between the Products and Used Amount of Mg (DADC; 24.75 mmol ECA; 8.16 mmol)

Table V. Various Alkyl Halides with Mg as Catalyst

| Mg (mmol) | Alkyl Halide | (mmol) | Temp. (°C) | Time (hr) | Yield of products[a] (%) 1 | 2 | 5 | 6 | Total |
|---|---|---|---|---|---|---|---|---|---|
| 51.44 | $ClCH_2COOEt$ | 8.2 | 160—180 | 0.3 | 30.1 | 4.1 | 5.6 | 1.5 | 41.3 |
| 51.44 | $CH_3(Cl)CHCOOEt$ | 7.3 | 160—180 | 0.5 | 28.3 | 6.6 | 3.6 | 2.7 | 41.2 |
| 51.44 | $ClCH_2CH_2COOEt$ | 7.3 | 180 | 0.7 | 1.8 | 23.1 | — | 2.4 | 27.3 |
| 51.44 | $ClCH_2COCH_3$ | 10.8 | 140—160 | 0.5 | 39.4 | 0.6 | 5.4 | 0.4 | 45.8 |
| 51.44 | $ClCH_2OEt$ | 10.6 | 90—140 | 0.5 | — | — | — | — | — |
| 51.44 | $ClCH_2CH_2OCH_2CH_2Cl$ | 7.0 | 160—180 | 0.5 | 2.3 | 24.2 | — | 4.1 | 30.6 |
| 51.44 | $ClCH_2(CH_2)_6CH_3$ | 6.7 | 180 | 1.0 | 1.8 | 25.4 | — | 2.7 | 29.9 |
| 51.44 | $ClCH_2COOEt$ | 0.4 | 180 | 3.0 | 1.1 | 33.0 | 0.8 | 5.1 | 40.0 |
| 51.44 | $ClCH_2(CH_2)_6CH_3$ | 0.3 | 180 | 3.0 | — | 28.4 | — | 5.9 | 34.3 |

a) Each yield was obtained from 24.75 mmol of DADC.

the yield of these orsellinic acids and the amount of ECA with a fixed amount of magnesium powder (51.14 mmol for 24.75 mmol of DADC), while Fig. 3 shows the relatoinship between the yield of orsellinic acids and the amount of magnesium with a fixed amount of ECA (8.16 m mol for 24.75 mmol of DADC). ECA was always effective for the formation of orsellinic acids, but the structural specificity of ECA molecule for a catalyst activity and the role of ECA for the condensation of DADC are not clear. Therefore, some of alkyl halides were tested in place of ECA in this reaction, and its results are shown in Table V. It was found that alkyl halides having α-chlorocarbonyl group in its molecule were effective as a catalyst for the formation of **1**, for example ethyl 2-chloropropionate and monochloroacetone, and that monochloroacetone was the most effective. Other alkyl halides exerted to yield not **1** but **2**. Some of alkyl halides with a low boiling point (below 140°) were not effective to give condensed products.

According to these findings, when magnesium and ECA are used as a catalyst, the sum of the yield of the products may be defined by the following equation:

$$P(1) + P(2) = 5 \text{ mmol}$$

where P (**1**) and P (**2**) are the amount (in mmol) of **1** and **2** obtained by the condensation of 5.0 g (24.75 mmol) of DADC. P (**1**) depends on the amount of magnesium and ECA. The reaction mechanism for the formation of **1** seemed to be similar to the type of a general enzymic reaction. For instance in the Michaelis-Menten equation,

$$M + E \longrightarrow [M\text{–}E] \xrightarrow{S} [M\text{–}E\text{–}S] \longrightarrow P + [M\text{–}E]$$

a complex of magnesium (M) and ECA (E) is regarded as a metalloenzyme (M–E), which is formed as an intermediate in this reaction. DADC is regarded as a substrate (S), and orsellinic acids are as products (P). Therefore P (**1**) is proportional to the concentration of the metalloenzyme (the amount of magnesium-ECA complex). On the contrary, P (**2**) is considered to be independent of the amount of catalyst.

According to our present studies, **2** was formed a little by heating DADC with no catalyst, while formation of **1** required a definite quantity of alkyl halide and magnesium, and the alkyl halide has a structural specificity. It is assumed that the mechanism of the products, **1** and **5**, may differ from that of **2** and **6**.

Further studies on the reaction mechanism for the formation of these products will be reported in the near future.

## Experimental[4]

**Condensation of DADC**——DADC was heated in an oil bath with mechanical stirrer using the catalyst shown in Tables. After the reaction was completed, the reaction mixture was acidified with dil. HCl and extracted with AcOEt. The AcOEt layer was washed with $H_2O$ and dried over $MgSO_4$. The AcOEt solution was used for the preparation of GC samples.

**Gas-Liquid Chromatography**——Apparatus and Condition: A Shimadzu Model GC-6AM gas chromatograph equipped with a flame ionization detector was used. The operating condition used for GC experiment were as follows: Liquid phase OV-1 (1.5%); solid support, 60—80 mesh Chromosorb W, AW-DMCS treated; column, 1.5 m × 3 mm, glass; initial temperature, 175°, final temperature, 240°, program rate 5°/min; injection and detector port temperature 260°; carrier gas ($N_2$) flow-rate, 40 ml/min; hydrogen flow-rate, 50 ml/min; air flow-rate, 0.8 l/min.

Preparation of GC Samples: One-fifth of the AcOEt solution described above was methylated with an excess of $CH_2N_2$ by the usual method, until the reactant gave a negative reaction to the $FeCl_3$ test. The solvent was evaporated and the residue was dissolved in AcOEt and made up to 50 ml. Pyrene was used as an internal standard. Five ml of this solution and 1 ml of pyrene solution (1.5 mg/ml in AcOEt) were pippeted

4) Melting point were determined on a hot plate using Yanagimoto micro-melting point apparatus and are uncorrected. NMR and mass spectral measurements were made with Hitachi Model R-22 Spectrometer using tetramethylsilane as an internal standard and on Shimadzu Model LKB-9000 spectrometer respectively.

into a 10 ml measuringflask and the whole was diluted with AcOEt to 10 ml. One μl of this solution was injected into the gas chromatograph.

**Calibration Curves**——All the methylated compounds used as the authentic standards were purified by column chromatography (silica gel-$CHCl_3$). Area ratio of each standard to pyrene was plotted against each concentration.

The Compounds used for Identification: Ethyl 3,5-dimethyl-4-methoxycarbonylorsellinate (methylated compound of **5**) and diethyl 3-hydroxy-5-methoxyhomophthalate (methylated compound of **6**) were synthesized from the new compound **5** and **6** as follows.

**Ethyl 4-Carboxyorsellinate (5)**——This compound was separated from the reaction mixture of the condensation product. A mixture of DADC (5.0 g), Mg (1.25 g), and ECA (1.0 g) was refluxed for 20 min at 160—180°. The reaction mixture was acidified with dil. HCl and extracted with AcOEt. The AcOEt layer was washed with $H_2O$, dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography over silica gel with benzene–petr. ether (1: 1) to give 0.3 g of **5** as colorless needles, mp 111—113°. *Anal.* Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 5.04. Found: C, 54.73; H, 5.08. NMR (in $d_6$-DMSO) $\delta$: 1.43 (3H, t, $J$=8 Hz, $CH_2C\underline{H}_3$), 2.52 (3H, s, $CH_3$), 4.45 (2H, q, $J$=8 Hz, $C\underline{H}_2CH_3$), 6.25 (1H, s, aromatic H), 11.70—12.00 (3H, broad, OH and COOH). MS *m/e*: 240 ($M^+$), 222 ($M^+-H_2O$), 176 ($M^+-H_2O$–EtOH).

**Ethyl 3,5-Dimethoxy-4-methoxycarbonylorsellinate (5′)**——**5** (0.5 g) was methylated with $CH_2N_2$ by the usual method and chromatographed over silica gel with $CHCl_3$ as an eluant. The eluate gave 0.51 g (87%) of **5′** as colorless needles, mp 60—61°. *Anal.* Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.48; H, 6.47. NMR (in $CDCl_3$) $\delta$: 1.32 (3H, t, $J$=8 Hz, $OCH_2C\underline{H}_3$), 2.23 (3H, s, $CH_3$), 3.72 (3H, s, $OCH_3$), 3.75 (3H, s, $OCH_3$), 3.77 (3H, s, $OCH_3$), 4.24 (2H, q, $J$=8 Hz, $OC\underline{H}_2CH_3$), 6.38 (1H, s, aromatic H). MS *m/e*: 282 ($M^+$), 251 ($M^+-OCH_3$), 237 ($M^+-OEt$), 236 ($M^+-EtOH$).

**Diethyl 3-Hydroxy-5-methoxyhomophthalate (6′)**——Diethyl 3,5-dihydroxyhomophthalate[2] (450 mg) was methylated with $CH_2N_2$ by the usual method and recrystallized from cyclohexane to give 450 mg of diethyl 3-hydroxy-5-methoxyhomophthalate (**6′**) as colorless needles, mp 60—62°. *Anal.* Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.51; H, 6.50. NMR (in $CDCl_3$) $\delta$: 1.22 (3H, t, $J$=7 Hz, $CH_2C\underline{H}_3$), 1.34 (3H, t, $J$=7 Hz, $CH_2C\underline{H}_3$), 3.79 (3H, s, $OCH_3$), 3.83 (2H, s, $CH_2COO$), 4.11 (2H, q, $J$=7 Hz, $CH_2COOC\underline{H}_2CH_3$), 4.34 (2H, q, $J$=7 Hz, $C\underline{H}_2CH_3$), 6.26 (1H, d, $J$=2 Hz, aromatic H), 6.41 (1H, d, $J$=2 Hz, aromatic H), 11.74 (1H, s, OH). MS *m/e*: 282 ($M^+$), 237 ($M^+-OEt$), 236 ($M^+-EtOH$).

Chemical and physical parameters were measured to confirm the structure of other methylated compounds of **1**, **2**, **3**, and **4** as follows.

**Diethyl 3,5-Dimethoxy-4-methoxycarbonylhomophthalate (1′)**——Heavy oil. *Anal.* Calcd. for $C_{17}H_{22}O_8$: C, 57.62; H, 6.26. Found: C, 57.19; H, 6.26. NMR (in $CDCl_3$) $\delta$: 1.20 (3H, t, $CH_2C\underline{H}_3$), 1.29 (3H, t, $CH_2C\underline{H}_3$), 3.67 (3H, s, $OCH_3$), 3.77 (3H, s, $OCH_3$), 3.78 (2H, s, $CH_2COO$), 3.83 (3H, s, $OCH_3$), 4.08 (2H, q, $C\underline{H}_2CH_3$), 4.28 (2H, q, $C\underline{H}_2CH_3$), 6.55 (1H, s, aromatic H). MS *m/e*: 354 ($M^+$).

**Diethyl 3,5-Dimethoxy-4-ethoxycarbonylhomophthalate (2′)**——Colorless needles from MeOH, mp 52—54°. *Anal.* Calcd. for $C_{18}H_{24}O_8$: C, 58.69; H, 6.57. Found: C, 58.64; H, 6.50. NMR (in $CCl_4$) $\delta$: 1.20 (3H, t, $CH_2C\underline{H}_3$), 1.26 (3H, t, $CH_2C\underline{H}_3$), 1.27 (3H, t, $CH_2C\underline{H}_3$), 3.55 (3H, s, $OCH_3$), 3.76 (3H, s, $OCH_3$), 3.78 (2H, s, $CH_2COO$), 4.04 (2H, q, $C\underline{H}_2CH_3$), 4.24 (2H, q, $C\underline{H}_2CH_3$), 4.26 (2H, q, $C\underline{H}_2CH_3$), 6.51 (1H, s, aromatic H). MS *m/e*: 368 ($M^+$).

**6-Ethoxycarbonyl-2,5,7-trimethoxychromone**——Colorless needles from dil. MeOH, mp 155°. NMR (in $CDCl_3$) $\delta$: 1.35 (3H, t, $J$=7 Hz, $CH_2C\underline{H}_3$), 3.82 (3H, s, $OCH_3$), 3.86 (3H, s, $OCH_3$), 3.91 (3H, s, $OCH_3$), 4.34 (2H, q, $J$=7 Hz, $C\underline{H}_2CH_3$), 5.46 (1H, s, $C_3H$), 6.62 (1H, s, $C_8H$). MS *m/e*: 308 ($M^+$), 290, 279, 263 ($M^+-OEt$. base peak), 262, 261, 249, 233. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1720 (C=O), 1650 (C=O).

**6-Ethoxycarbonyl-4,5,7-trimethoxycoumarin**——Colorless needles from MeOH, mp 185°. NMR (in $CDCl_3$) $\delta$: 1.35 (3H, t, $J$=7 Hz, $CH_2C\underline{H}_3$), 3.83 (3H, s, $OCH_3$), 3.87 (3H, s, $OCH_3$), 3.89 (3H, s, $OCH_3$), 4.40 (2H, q, $J$=7 Hz, $C\underline{H}_2CH_3$), 5.59 (1H, s, $C_3H$), 6.67 (1H, s, $C_8H$). MS *m/e*: 308 ($M^+$), 263 ($M^+-OEt$). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1730 (C=O), 1715 (C=O).